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COMPLETE SPECIFICATION

Polymeric Compositions

We EASTMAN KODAK COMPANY, a Company organized under the Laws of the State of New Jersey, United States of America, of 343, State Street, Rochester, New York 14650, United States of America, (Assignee of HARRY WESLEY COOVER, JR. and RICHARD LEON MCCONNELL), do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to the compounding of homo- and copolymers with various pigments, extenders, dyes and fillers, all of which may be grouped under the term "additives". More particularly it relates to the use of additive concentrates in the compounding process for improving the dispersions of the additives in the polymers.

Polyolefines such as polyethylene and polypropylene are conventionally compounded with various types of additives for a variety of purposes. For example, dispersions of carbon black in polyethylene is known to retard oxidative degradation while dispersions of coloured pigments such as cadmium yellow therein impart desirable colours. Whether the additive be for colouring, filling, extending, oxidation retardation or other purposes, a uniform dispersion thereof in the polymer is necessary for maximum development of desired properties. For example, improved pigment dispersions provide improved weatherability, deeper colour shades for a given overall pigment concentration and greater processing ease in such procedures as the spinning of pigmented fibres and the moulding of bulk plastic.

It has now been found possible to provide improved means for facilitating the dispersal of additives in polymers and particularly a commercially useful process for improving the homogeneity of additive dispersions in polyolefines. Such a process is applicable to the difficultly compounded polyolefines.

According to the present invention there is provided a polymeric composition which comprises a main polymer and a concentrate comprising at least one carrier which is poly-1-butene or a copolymer of 1-butene and at least one other copolymerizable monomer, the carrier containing a dispersed additive in an amount of at least 5% by weight and the main polymer is different from the carrier. Preferably the amount of dispersed additive is 10 to 90% by weight.

The present invention also provides moulded products, shaped products and fibres obtained from the compositions of the present invention.

The present invention further provides a method of uniformly dispersing an additive in a main polymer which comprises blending the concentrate with the main polymer.

In one embodiment the method of the present invention involves dispersing the additive in the carriers to form the concentrate and then blending the concentrate with the polymeric material.

Thus, it has been found that the homopolymer of 1-butene and copolymers of 1-butene and certain other monomers act as excellent medium for carrying various additives and dispersing them in other polymers. Monomers such as ethylene, propylene, 1-pentene, 1-hexene and 4-methyl-1-pentene can be copolymerized with 1-butene to provide copolymers useful as master batch materials. It is apparent, moreover, to one skilled in the art that a large variety of α-olefine or diene comonomers containing from 1 to 18 carbon atoms are copolymerizable with 1-butene without destroying the beneficial effect of the 1-butene component in carrying the additive. Naturally, as the pro-

[*Price 4s. 6d.*]

portion of these other comonomers is increased, the effect of the 1-butene is correspondingly diminished and a proper balance for the particular application should be determined by routine investigation. In general, it may be said that the preferred copolymers would contain 75 to 99% 1-butene but copolymers containing as little as 20% 1-butene would be operable to a degree at least. Poly-1-butene master batches containing from 10 to 60% by weight of additives have been found to produce excellent dispersions thereof in homo- and copolymers of α-olefines and vinyl polymers such as polystyrene.

The poly-1-butene is conventionally made by the polymerization of 1-butene to stereoregular polymer in the presence of conventional co-ordination catalysts. The molecular weight of the poly-1-butene is not critical and inherent viscosities ranging from about 0.2 to about 5.0 have been successfully employed. While the hydrocarbon solvent extractable portion of the poly-1-butene polymer may be employed, it is preferred to use the crystalline portion or at least the total polymer formed, i.e., the unseparated amorphous and crystalline portions.

The concentrates used in the present invention are readily prepared by blending the additive with poly-1-butene powder, granules or pellets in conventional equipment, such as Henschell mixers, Banbury mixers, extrusion equipment and hot rolls used for blending various agents with plastic materials. The presence of further additives such as stabilizers, antioxidants, plasticizers, and lubricants normally used in polyolefines does not significantly detract from the beneficial properties of the poly-1-butene master batch. The master batches may be used in the form of powder, granules or pellets and may be blended with polyethylene and/or polypropylene and the other polymeric materials in the conventional equipment mentioned above.

Typical of the additives which may be used in the present invention are carbon black, calcium carbonate, magnesium carbonate, silicon dioxide, asbestos, china clay, zinc oxide, iron oxide, lignin, anthracite coal, bituminous coal, silicates, wood dust, cork dust, cellulose and colouring agents.

The present invention may be illustrated by but is in no manner limited to the following Examples:

Example 1

Poly-1-butene (I.V. of 2.5) was blended with 25% by weight of the following additives:

Black Pearl 71 (carbon black)
Phthalocyanine Green
Phthalocyanine Blue
Asbestos
Calcium Carbonate
Cab-O-Sil (silica)
Anthracite Coal
Bituminous Coal
Iron Oxide
Cellulose
Cork Dust
Cadmium Yellow
Cadmium Red
Benzidine Yellow
*Monarch 81 (carbon black)
*Monarch 74 (carbon black)
*Sterling L (carbon black)
Azulene
N-nitrosodiethylamine

* "Black Pearl", "Monarch" and "Sterling" are Trade Marks.

These blends contained 0.4% by weight dilauryl thiodipropionate and 0.1% by weight 4,4'-butylidene bis(6-tert.butyl m-cresol) to prevent degradation of the polymer during the blending and subsequent moulding operations. The dispersions of the above additives were excellent. Similar excellent dispersions were obtained using 10%, 20%, 40%, 50% and 60% by weight of the additives. Master batches were also prepared using poly-1-butene having an I.V. of 0.2, 0.8, 1.2, 1.5, 1.7, 2.0, 3.5 and 5.0. All gave concentrates containing excellent dispersions of the additives.

Example 2

The above 25% by weight Black Pearl 71 carbon black master batch was blended with polypropylene (I.V.=2.0) to give a concentration of 3% by weight carbon in the polymeric blend. When a small pellet was melted between two glass plates into a thin film, it was readily apparent that the carbon black was uniformly distributed. The dispersion had an A rating (excellent) according to Western Electric standards (Western Electric Manufacturing Standard 17,000: Section 1059). In comparison, when a polypropylene master batch containing 25% by weight carbon was blended with additional polypropylene to yield a 3% by weight concentration of carbon black, the dispersion was poor (D rating according to Western Electric standards).

The physical properties of a polypropylene homopolymer containing 3% by weight carbon black and prepared from the poly-1-butene master batch are compared with unpigmented polypropylene in the following table:

Property	Polypropylene	Polypropylene Containing 3% Carbon
Melt Flow	1.9	1.8
Inherent Viscosity of Moulded Specimen	2.0	2.0
Durometer Hardness	72	75
Izod Impact Strength, Notched (23°C.)	0.5	0.5
Izod Impact Strength, Unnotched (23°C.)	23	22
Brittleness Temperature, °C.	−4	−2
Stiffness, psi	175,000	185,000

This data demonstrates an improvement in stiffness and no embrittlement of the polymer. Similar results were achieved when the other carbon black master batches in poly-1-butene were blended with polypropylene.

EXAMPLE 3

The 20% by weight Black Pearl 71 master batch described in Example 1 was blended with low-density polyethylene in a Banbury mixer to provide a composition containing 2% by weight carbon black. The dispersion of carbon black was excellent and moulded objects were uniform in colour. This polymer had excellent resistance to the effects of sunlight and was not brittle. Similar results were achieved when the poly-1-butene carbon black master batches were blended with medium and also high-density polyethylene. The dispersions were much better than those prepared with conventional polyethylene carbon black master batches.

EXAMPLE 4

The poly-1-butene master batches containing 25 and 50% by weight calcium carbonate were blended with polyethylene, polypropylene and an 80/20 propylene/1-butene copolymer to provide uniformly white compositions having excellent physical properties, there being 5% and 10% by weight, respectively, of the calcium carbonate in the compositions.

EXAMPLE 5

The poly-1-butene master batch containing 20% phthalocyanine blue was blended with polypropylene to provide a concentration of 2% by weight pigment in the polypropylene. The pigmented polypropylene was spun into fibres which were quite uniform in colour and had excellent physical properties. Similar results were obtained when the phthalocyanine green and carbon black master batches were blended with either polyethylene, polypropylene or a 90/10 propylene/1-butene copolymer and spun into fibres.

EXAMPLE 6

The poly-1-butene master batch containing 20% Cadmium Red was blended with polystyrene to provide a concentration of 0.5% by weight pigment in the polystyrene. When this polymer was moulded into cups, the cups were uniformly coloured. Similar results were obtained when the final concentrations of pigment in the polystyrene were 5% and 10%.

EXAMPLE 7

A poly-1-butene carbon black master batch containing 50% by weight carbon was blended with an ethylene/propylene copolymer rubber (I.V.=1.9) containing 60 mole percent ethylene to provide a final concentration of 20% by weight carbon in the blend. The dispersion of carbon black was uniform. Similar good dispersions were obtained when other ethylene/propylene, ethylene/1-butene or propylene/1-butene copolymers rubbers were used. Good dispersions were also achieved when benzidine yellow, phthalocyanine green, phthalocyanine blue, and Cadmium Red master batches were blended with three copolymer rubbers to provide a final concentration of colouring agent of 0.2 to 10% by weight.

EXAMPLE 8

A poly-1-butene master batch containing 40% by weight asbestos was blended with polypropylene to yield a final blend containing 20% by weight asbestos. Moulded objects from this blend were quite rigid and had excellent impact strength.

EXAMPLE 9

A 1-butene/propylene copolymer containing 90% by weight 1-butene was blended with 40% by weight of Black Pearl 71 (carbon black). Excellent dispersions of carbon black were achieved when this master batch was blended with either polypropylene or polyethylene to give a concentration of 5% by weight carbon black in the composition.

Similarly good results were obtained when master batches of phthalocyanine blue in 1-butene/propylene copolymers were dispersed in polypropylene and polyethylene.

WHAT WE CLAIM IS:—

1. A polymeric composition which comprises a main polymer and a concentrate comprising at least one carrier which is poly-1-butene or a copolymer of 1-butene and at least one other copolymerizable monomer, the carrier containing a dispersed additive in

an amount of at least 5% by weight and the main polymer being different from the carrier.

2. A composition as claimed in claim 1 in which the concentrate contains from 10% to 90% by weight of dispersed additive.

3. A composition as claimed in claim 2 in which the concentrate contains from 10% to 60% by weight of dispersed additive.

4. A composition as claim in any of claims 1 to 3 in which the carrier is poly-1-butene.

5. A composition as claimed in claim 4 in which the poly-1-butene is obtained by polymerization of 1-butene to a stereoregular polymer in the presence of a co-ordination catalyst.

6. A composition as claimed in any of claims 1 to 3 in which the carrier is a copolymer of 1-butene and an α-olefine or diene containing 1 to 18 carbon atoms.

7. A composition as claimed in claim 6 in which the α-olefine is ethylene, propylene, pentene, 1-hexene or 4-methyl-1-pentene.

8. A composition as claimed in claim 6 or 7 in which the copolymer contains 75 to 99% by weight 1-butene.

9. A composition as claimed in any of claims 1 to 8 in which the main polymer is a polymer or copolymer of an α-olefine.

10. A composition as claimed in claim 9 in which the main polymer is polyethylene, polypropylene or a mixture of polyethylene and polypropylene.

11. A composition according to claim 1 substantially as hereinbefore described with particular reference to any of Examples 2 to 9.

12. A method for uniformly dispersing an additive in a main polymer which comprises blending the main polymer with a concentrate as defined in any of claims 1 to 8.

13. A method as claimed in claim 12 which comprises dispersing the additive in poly-1-butene or a copolymer of 1-butene and at least one other copolymerizable monomer to form a concentrate as defined in any of claims 1 to 8 and then blending the concentrate with the main polymer.

14. A method as claimed in claim 12 or 13 in which the main polymer is a polymer or copolymer of an α-olefine.

15. A method as claimed in claim 14 in which the main polymer is polyethylene, polypropylene or a mixture of polyethylene and polypropylene.

16. A method according to claim 12 for uniformly dispersing an additive in a main polymer substantially as hereinbefore described with particular reference to any of Examples 2 to 9.

17. Shaped products whenever obtained from a composition as claimed in any of claims 1 to 11.

18. Moulded products whenever obtained from a composition as claimed in any of claims 1 to 11.

19. Fibres whenever obtained from a composition as claimed in any of claims 1 to 11.

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